

# Water-emulsifiable isocyanates with improved properties

The invention relates to water-emulsifiable isocyanates  
5 possessing improved emulsifiability and featuring increased  
hardness of coatings obtained using them, to processes for  
preparing them, and to their use.

Water-emulsifiable polyisocyanates are added as crosslinking  
10 agents to aqueous polymer dispersions and have been widely  
described in the literature. Emulsifiability in water is brought  
about by blending the polyisocyanates with emulsifiers which are  
obtained by reacting the polyisocyanates with hydrophilic  
molecules.

15 Hydrophilic molecules commonly used include nonionic hydrophilic  
molecules such as polyalkylene oxide alcohols.

EP-A2 206 059 describes water-dispersible polyisocyanate  
20 formulations comprising an aliphatic polyisocyanate and a  
reaction product of an aliphatic polyisocyanate with a monohydric  
or polyhydric, nonionic polyalkylene ether alcohol emulsifier  
which has at least one polyether chain containing at least 10  
ethylene oxide units. As suitable polyisocyanates, extensive  
25 lists are given of aliphatic and cycloaliphatic diisocyanates,  
more preferably isocyanurates and biurets based on  
1,6-diisocyanatohexane (HDI) and/or isocyanurates based on  
1-isocyanato-3,5,5-trimethyl-5-isocyanatomethylcyclohexane  
(IPDI).

30 EP-A1 540 985 likewise describes polyisocyanate mixtures, but in  
this case the polyether chains have an average ethylene oxide  
unit content of from 5.0 to 9.9.

35 EP-A2 486 881 describes nonaqueous aliphatic polyisocyanate  
formulations comprising polyisocyanates from a list of aliphatic  
polyisocyanates and comprising an amount, sufficient to ensure  
the dispersibility of the aliphatic polyisocyanate, of a reaction  
product of an aromatic or aliphatic diisocyanate and a monohydric  
40 or polyhydric polyalkylene ether alcohol having at least 8  
ethylene oxide units in the polyether chain.

DE-A1 199 58 170 describes polyether-modified, water-dispersible  
polyisocyanate mixtures which have been modified with monohydric  
45 polyalkylene oxide polyether alcohols. Very particular preference  
is given to polyisocyanates or polyisocyanate mixtures with an

isocyanurate structure based on HDI, IPDI and/or 4,4'-diisocyanatodicyclohexylmethane.

DE-A1 198 22 890 describes aqueous two-component polyurethane  
5 coating systems whose hardener component is prepared from polyalkylene oxide polyether alcohols and aliphatically and/or cycloaliphatically attached isocyanate groups, preferably isocyanurate structures based on HDI, IPDI and/or 4,4'-diisocyanatodicyclohexylmethane, under allophanatization  
10 conditions. The predominant attachment of polyether chains by way of allophanate groups is also known from DE-A1 198 47 077.

Nonionic emulsifiers described include polyvinylpyrrolidone-modified polyisocyanates (EP-A2 754 713).

15 Also in use as actively dispersing units are polyalkylene oxide ethers containing carboxylic acid groups, as described in DE-A1 100 07 820 and DE-A1 41 13 160, or polyether ester alcohols (EP-A1 728 785).

20 DE-A1 40 01 783 describes polyisocyanate mixtures which, with a uretdione content of 1 to 23% by weight, contain chemically bonded carboxyl groups for dispersibility.

25 Furthermore, carboxyl-containing compounds are described as emulsifiers (EP-A2 548 669), tertiary amino and/or ammonium groups (EP-A1 582 166 and EP-A1 531 820), acidic esters of phosphoric acid (DE-A1 197 24 199) or sulfonic acids (EP-A1 703 255).

30 A disadvantage of the polyisocyanate mixtures described is that they do not meet the requirements imposed on the hardness of the coatings obtainable using them.

35 Water-emulsifiable isocyanates can be dissolved in organic solvents such as, for example, carbonic esters or lactones for the purpose of improving dispersibility, as described in EP-A 697 424.

40 From "Lackharze" [Resins for Coatings] (edited by D. Stoye and W. Freitag, Hanser 1996, p. 195) it is known that IPDI trimer, which gives resins for coatings a comparatively high level of hardness, even going as far as brittleness, is frequently employed in blends with HDI derivatives in order to lessen the hardness.

Users require the water-emulsifiable isocyanates to have the following properties:

1. The isocyanate should be easy to emulsify; having to use demanding apparatus such as high-shear stirring elements is deprecated.
2. The emulsion should be fine, since otherwise the gloss may be disrupted or turbidity may appear, for example.
3. In the case of coatings, a frequent desire is for a high ultimate hardness.
4. The ultimate hardness should be attained as quickly as possible.

It is an object of the present invention to provide water-emulsifiable polyisocyanates which exhibit improved emulsifiability properties and with which it is possible to produce coatings having high hardness, rapid increase in hardness, and enhanced emulsifiability at the same time.

We have found that this object is achieved by mixtures comprising

(A) an isocyanurate and/or biuret of 1,6-diisocyanatohexane (HDI),

(B) an isocyanurate of 1-isocyanato-3,5,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI),

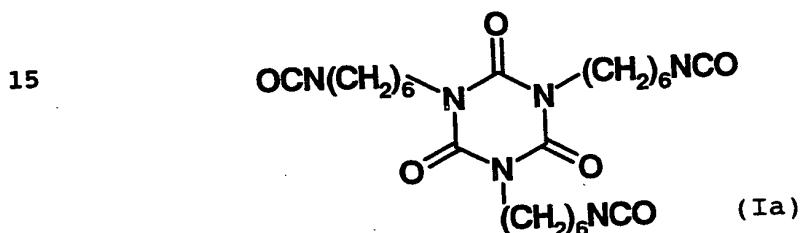
(C) at least one emulsifier, obtainable by reacting at least one diisocyanate (C2) selected from tetramethylene diisocyanate, hexamethylene diisocyanate (HDI), dodecamethylene diisocyanate, 1,4-diisocyanatocyclohexane, 4,4'-di(isocyanatocyclohexyl)methane, trimethylhexane diisocyanate, tetramethylhexane diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-(isocyanatomethyl)cyclohexane (IPDI), 2,4- or 2,6-tolylene diisocyanate and the isomer mixtures thereof, tetramethylxylylene diisocyanate, p-xylylene diisocyanate, 2,4'- or 4,4'-diisocyanatodiphenylmethane with at least one component (C1) containing at least one group which is reactive toward isocyanate groups and containing at least one hydrophilic group, and

(D) if desired, solvent.

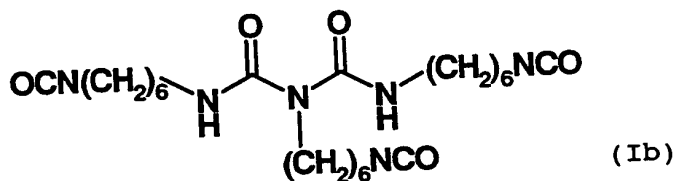
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The mixtures of the invention prove readily emulsifiable, lead to a fine, stable emulsion, and can be used to give coatings which exhibit a rapid increase in hardness and a high ultimate hardness.

- 5 Polyisocyanates (A) are isocyanurates (A1) and/or biurets (A2) of 1,6-diisocyanatohexane (HDI). In accordance with the invention this includes those polyisocyanates composed to an extent of at least 50% by weight, preferably at least 66%, more preferably at  
 10 least 75%, very preferably at least 85%, and in particular at least 95% by weight, of compounds of the formula (Ia) and/or (Ib),



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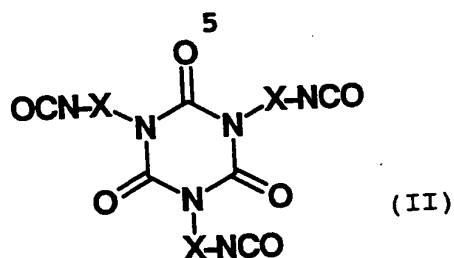


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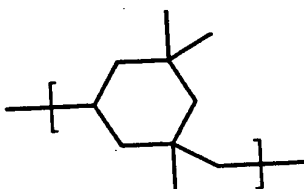
and their higher homologues.

- The composition of the polyisocyanates, i.e., for example, the  
 30 fractions of isocyanurates and/or biurets and their higher homologues, and the average functionality are determined in this specification by gel permeation chromatography using polystyrene as standard and tetrahydrofuran as eluent.

- 35 Polyisocyanates (B) are isocyanurates of 1-isocyanato-3,5,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI). In accordance with the invention, this includes those polyisocyanates which are composed to an extent of at least 50% by weight, preferably at least 66%, more preferably at least 75%,  
 40 very preferably at least 85%, and in particular at least 95% by weight, of the compound of the formula (II),



in which X is



15 and their higher homologues.

20 Suitable emulsifiers (C) in accordance with the invention are compounds obtainable by reacting at least one diisocyanate (C2) with at least one, preferably 1 to 2, particularly preferably one component (C1) containing at least one group which is reactive toward isocyanate groups and containing at least one hydrophilic group. (C1) is referred to below as "hydrophile".

25 Examples of isocyanate-reactive groups are hydroxyl groups (-OH), unsubstituted or monosubstituted amino groups or mercapto groups (-SH), preferably hydroxyl groups.

30 Generally, therefore, the emulsifiers (C) contain component (C1) in chemically attached form.

The components (C1) may, for example, comprise compounds such as are known in the prior art: for example, from the prior art cited 35 in the introduction.

In particular, these may be compounds which contain at least one isocyanate-reactive group and

- 40 - (C1a) at least one cationic hydrophilic group,  
 - (C1b) at least one anionic hydrophilic group or  
 - (C1c) at least one nonionic hydrophilic group.

45 Preferred compounds (C1) contain 1 to 3 isocyanate-reactive groups and 1 to 3 hydrophilic groups, more preferably 1 to 2 isocyanate-reactive groups and 1 to 2 hydrophilic groups, and

very preferably one isocyanate-reactive group and one hydrophilic group.

Compounds (C1a) contain at least one isocyanate-reactive group  
5 and at least one cationic hydrophilic group or at least one  
hydrophilic group which can be converted into a cationic group,  
and are, for example, compounds such as those described in  
EP-A1 582 166, especially from page 5 line 42 to page 8 line 22  
and in particular from page 9 line 19 to page 15 line 34 therein,  
10 or in EP-A1 531 820, especially from page 3 line 21 to page 4  
line 57 therein, or in DE-A1 42 03 510, especially from page 3  
line 49 to page 5 line 35 therein. Those documents are explicitly  
incorporated into the present disclosure content by reference.

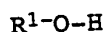
15 Compounds (C1b) contain at least one isocyanate-reactive group  
and at least one anionic hydrophilic group or at least one  
hydrophilic group which can be converted into an anionic group,  
and are, for example, compounds as described in EP-A1 703 255,  
especially from page 3 line 54 to page 4 line 38 therein, in  
20 DE-A1 197 24 199, especially on page 3 lines 4 to 30 therein, in  
DE-A1 40 10 783, especially column 3 lines 3 to 40 therein, in  
DE-A1 41 13 160, especially from column 3 line 63 to column 4  
line 4 therein, and in EP-A2 548 669, especially from page 4 line  
50 to page 5 line 6 therein. Those documents are expressly hereby  
25 incorporated into the present disclosure content by reference.

Compounds (C1c) contain at least one isocyanate-reactive group  
and at least one nonionic hydrophilic group and are for example  
compounds as described in EP-A2 754 713, especially on page 3  
30 lines 31 to 51 therein, in EP-A2 206 059, especially on page 8  
line 33 to page 9 line 26 therein, in EP-A2 486 881, especially  
on page 2 lines 42 to 54 therein, in EP-A1 540 985, especially on  
page 4 lines 43 to 58 therein, in EP-A1 728 785, especially on  
page 4 line 55 to page 5 line 54 therein, in EP-A1 959 115,  
35 especially on page 4 lines 23 to 46 therein, in DE-A1 199 58 170,  
especially on page 4 lines 22 to 48 therein, and in DE-A1 100 07  
820, especially from page 4 line 10 to page 5 line 12 therein.  
Those documents are hereby expressly incorporated into the  
present disclosure content by reference.

40 The hydrophiles (C1) are preferably compounds (C1c) containing at  
least one isocyanate-reactive group and at least one nonionic  
hydrophilic group.

Particularly preferred hydrophiles (C1c) are polyalkylene oxide polyether alcohols obtainable by alkoxyating suitable initiator molecules.

- 5 Suitable initiator molecules for the preparation of monohydric polyalkylene oxide polyether alcohols are thiol compounds, monohydroxy compounds of the formula



10

or secondary monoamines of the formula



- 15 in which

$R^1$ ,  $R^2$ , and  $R^3$  independently of one another are each  $C_1-C_{18}$  alkyl,  $C_2-C_{18}$  alkyl uninterrupted or interrupted by one or more oxygen and/or sulfur atoms and/or by one or more substituted or unsubstituted imino groups, or are  $C_6-C_{12}$  aryl,  $C_5-C_{12}$  cycloalkyl  
20 or a five- or six-membered heterocycle containing oxygen, nitrogen and/or sulfur atoms, or  $R^2$  and  $R^3$  together form an unsaturated, saturated or aromatic ring whose members are uninterrupted or interrupted by one or more oxygen and/or sulfur atoms and/or by one or more substituted or unsubstituted imino  
25 groups, it being possible for the radicals mentioned each to be substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles.

- Preferably  $R^1$  is  $C_1$  to  $C_4$  alkyl, i.e., methyl, ethyl, iso-propyl,  
30 n-propyl, n-butyl, iso-butyl, sec-butyl or tert-butyl; very preferably  $R^1$  is methyl.

Examples of suitable monofunctional initiator molecules may be saturated monoalcohols such as methanol, ethanol, n-propanol,  
35 isopropanol, n-butanol, isobutanol, sec-butanol, the isomeric pentanols, hexanols, octanols and nonanols, n-decanol, n-dodecanol, n-tetradecanol, n-hexadecanol, n-octadecanol, cyclohexanol, cyclopentanol, the isomeric methylcyclohexanols or hydroxymethylcyclohexane, 3-ethyl-3-hydroxymethyloxetane, or  
40 tetrahydrofurfuryl alcohol; unsaturated alcohols such as allyl alcohol, 1,1-dimethylallyl alcohol or oleyl alcohol, aromatic alcohols such as phenol, the isomeric cresols or methoxyphenols, araliphatic alcohols such as benzyl alcohol, anisyl alcohol or cinnamyl alcohol; secondary monoamines such as dimethylamine,  
45 diethylamine, dipropylamine, diisopropylamine, di-n-butylamine, diisobutylamine, bis(2-ethylhexyl)amine, N-methyl- and N-ethylcyclohexylamine or dicyclohexylamine, heterocyclic

secondary amines such as morpholine, pyrrolidine, piperidine or 1H-pyrazole, and also amino alcohols such as 2-dimethylaminoethanol, 2-diethylaminoethanol, 2-diisopropylaminoethanol, 2-dibutylaminoethanol, 5 3-(dimethylamino)-1-propanol or 1-(dimethylamino)-2-propanol.

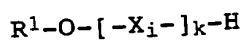
Alkylene oxides suitable for the alkoxylation reaction are ethylene oxide, propylene oxide, iso-butylene oxide, vinyloxirane and/or styrene oxide, which may be used in any order or else in a 10 mixture in the alkoxylation reaction.

Preferred alkylene oxides are ethylene oxide, propylene oxide, and mixtures thereof; particular preference is given to ethylene oxide.

15 Preferred compounds (C1c) are polyether alcohols based on polyalkylene oxide polyether alcohols prepared using saturated aliphatic or cycloaliphatic alcohols of the abovementioned type as initiator molecules. Very particular preference is given to 20 those based on polyalkylene oxide polyether alcohols prepared using saturated aliphatic alcohols having 1 to 4 carbon atoms in the alkyl radical. Polyalkylene oxide polyether alcohols prepared starting from methanol are especially preferred.

25 The monohydric polyalkylene oxide polyether alcohols contain on average generally from 5 to 35, preferably from 7 to 30, more preferably from 7 to 25, very preferably from 10 to 22, alkylene oxide units per molecule, in particular from 10 to 22 ethylene oxide units.

30 Preferred polyether alcohols (C1c) are, therefore, compounds of the formula



35 where

$R^1$  is as defined above,  
 $k$  is an integer from 5 to 35, preferably from 7 to 30, more 40 preferably from 7 to 25, and in particular from 10 to 22, and each  $X_i$  can be selected, independently of one another for  $i = 1$  to  $k$ , from the group consisting of  $-CH_2-CH_2-O-$ ,  $-CH_2-CH(CH_3)-O-$ ,  $-CH(CH_3)-CH_2-O-$ ,  $-CH_2-C(CH_3)_2-O-$ ,  $-C(CH_3)_2-CH_2-O-$ ,  $-CH_2-CHVin-O-$ ,  $-CHVin-CH_2-O-$ ,  $-CH_2-CHPh-O-$  and  $-CHPh-CH_2-O-$ , preferably from the 45 group consisting of  $-CH_2-CH_2-O-$ ,  $-CH_2-CH(CH_3)-O-$  and



-CH(CH<sub>3</sub>)-CH<sub>2</sub>-O-, and more preferably -CH<sub>2</sub>-CH<sub>2</sub>-O-  
where Ph is phenyl and Vin is vinyl.

The polyether alcohols may further contain, as hydrophilic  
5 synthesis components, minor amounts of other isocyanate-reactive  
compounds containing anionic or cationic groups - for example,  
with carboxylate, sulfonate or ammonium groups. This, however, is  
less preferred.

- 10 Diisocyanates (C2) are selected in accordance with the invention  
from the group consisting of tetramethylene diisocyanate,  
hexamethylene diisocyanate, dodecamethylene diisocyanate,  
1,4-diisocyanatocyclohexane, 4,4'-di(isocyanatocyclo-  
hexyl)methane, trimethylhexane diisocyanate, tetramethylhexane  
15 diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-(isocyanato-  
methyl)cyclohexane, 2,4- or 2,6-tolylene diisocyanate and the  
isomer mixtures thereof, tetramethylxylylene diisocyanate,  
p-xylylene diisocyanate, 2,4'- or 4,4'-diisocyanatodiphenyl-  
methane, and also a mixture of at least two of these  
20 diisocyanates. Preferably, however, one of these components or an  
isomer mixture is reacted.

- Particular preference is given to hexamethylene diisocyanate,  
4,4'-di(isocyanatocyclohexyl)methane, 1-isocyanato-3,3,5-tri-  
25 methyl-5-(isocyanatomethyl)cyclohexane, tetramethylxylylene  
diisocyanate, 2,4'- or 4,4'-diisocyanatodiphenylmethane and 2,4-  
or 2,6-tolylene diisocyanate and the isomer mixtures thereof,  
very particular preference to hexamethylene diisocyanate,  
1-isocyanato-3,3,5-trimethyl-5-(isocyanatomethyl)cyclohexane and  
30 2,4- or 2,6-tolylene diisocyanate, and especially 2,4- or  
2,6-tolylene diisocyanate and the isomer mixtures thereof.

- The diisocyanates are generally present to the extent of at least  
75 mol% as monomers, preferably to the extent of at least  
35 85 mol%, more preferably at least 90 mol%, and, with very  
particular preference, at least 95 mol%.

- To react the diisocyanates (C2) with the isocyanate-reactive  
compounds (C1) it is normal to use from 60 to 120 mol%,  
40 preferably from 80 to 120 mol%, more preferably from 90 to  
110 mol%, and in particular from 100 mol% of isocyanate-reactive  
groups in (C1) per mole of isocyanate groups in (C2).

10

To prepare the component which is active as emulsifier (C) the starting components (C1) and (C2) are reacted with one another at temperatures from 40 to 180°C, preferably 50 to 150°C, observing the specified molar ratio.

5

The reaction time is generally 10 min to 5 hours, preferably 15 min to 4 hours, more preferably 20 to 180 min, and very preferably 30 to 120 min.

10 In order to accelerate the reaction it is possible where appropriate to use suitable catalysts.

These are the customary catalysts which are known for these purposes, examples being metal carboxylates, metal chelates or  
15 tertiary amines of the type described in GB-A-0 994 890, alkylating agents of the type described in US-A-3 769 318, or strong acids as described by way of example in EP-A-0 000 194.

Suitable catalysts are, in particular, zinc compounds, such as  
20 zinc(II) stearate, zinc(II) n-octanoate, zinc(II) 2-ethyl-1-hexanoate, zinc(II) naphthenate or zinc(II) acetylacetonate, tin compounds, such as tin(II) n-octanoate, tin(II) 2-ethyl-1-hexanoate, tin(II) laurate, dibutyltin oxide, dibutyltin dichloride, dibutyltin diacetate, dibutyltin  
25 dilaurate, dibutyltin dimaleate or dioctyltin diacetate, aluminum tri(ethyl acetoacetate), iron(III) chloride, potassium octoate, manganese compounds, cobalt compounds or nickel compounds, and strong acids, such as trifluoroacetic acid, sulfuric acid, hydrogen chloride, hydrogen bromide, phosphoric acid or  
30 perchloric acid, for example, or any desired mixtures of these catalysts.

Suitable though less preferred catalysts for the process are also those catalysts as described for example in EP-A-0 649 866 on  
35 page 4 line 7 to page 5 line 15.

Preferred catalysts for the process of the invention are zinc compounds of the abovementioned type. Very particular preference is given to using zinc(II) n-octanoate, zinc(II)  
40 2-ethyl-1-hexanoate and/or zinc(II) stearate.

Where used, these catalysts are employed in an amount of from 0.001 to 5% by weight, preferably 0.005 to 1% by weight, based on the overall weight of the reactants.

45

The polyaddition reaction for preparing the polyurethane formulation of the invention may take place with particular preference in the presence of cesium salts, as described in the earlier German patent application of December 12, 2001 bearing the reference 10161156.0. Preferred cesium salts are compounds in which the following anions are employed:  $F^-$ ,  $Cl^-$ ,  $ClO^-$ ,  $ClO_3^-$ ,  $ClO_4^-$ ,  $Br^-$ ,  $I^-$ ,  $IO_3^-$ ,  $CN^-$ ,  $OCN^-$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ ,  $S^{2-}$ ,  $SH^-$ ,  $HSO_3^-$ ,  $SO_3^{2-}$ ,  $HSO_4^-$ ,  $SO_4^{2-}$ ,  $S_2O_2^{2-}$ ,  $S_2O_4^{2-}$ ,  $S_2O_5^{2-}$ ,  $S_2O_6^{2-}$ ,  $S_2O_7^{2-}$ ,  $S_2O_8^{2-}$ ,  $H_2PO_2^-$ ,  $H_2PO_4^-$ ,  $HPO_4^{2-}$ ,  $PO_4^{3-}$ ,  $P_2O_7^{4-}$ ,  $(OC_nH_{2n+1})^-$ ,  $(C_nH_{2n-1}O_2)^-$ ,  $(C_nH_{2n-3}O_2)^-$ , and  $(C_{n+1}H_{2n-2}O_4)^{2-}$ , n standing for numbers from 1 to 20.

Particularly preferred compounds are cesium carboxylates in which the anion is of the formula  $(C_nH_{2n-1}O_2)^-$  or  $(C_{n+1}H_{2n-2}O_4)^{2-}$  where n is from 1 to 20. Especially preferred cesium salts contain monocarboxylate anions of the formula  $(C_nH_{2n-1}O_2)^-$  where n stands for numbers from 1 to 20. Particular mention may be made here of formate, acetate, propionate, hexanoate, and 2-ethylhexanoate.

The cesium salts are used in amounts of from 0.01 to 10 mmol of cesium salt per kg of solvent-free reaction mixture. They are preferably used in amounts of from 0.05 to 2 mmol of cesium salt per kg of solvent-free reaction mixture.

The cesium salts can be added to the reaction mixture in solid form, but preferably in dissolved form. Suitable solvents are polar, aprotic solvents or else protic solvents. Particularly suitable besides water are alcohols; especially suitable are polyols, such as are also used as synthesis units for polyurethanes, such as ethane-, propane-, and butane-diols, for example. The use of the cesium salts makes it possible to carry out the polyaddition reaction under the customary conditions.

Addition to the reaction mixture may take place by any desired method. Thus, for example, it is possible to admix the catalyst (where used) either to the polyisocyanate component (A), (B), (C2) and/or to the emulsifier component (C1) before the beginning of the actual reaction. It is also possible to add the catalyst to the reaction mixture at any time during the reaction or else, in a two-stage reaction regime, following the urethanization, i.e., when the NCO content corresponding theoretically to complete conversion of isocyanate and hydroxyl groups has been reached.

The sequence in which components (A), (B), and (C) are mixed is not critical to the invention: for example, the components may be mixed with one another simultaneously, (C), or at least part of

it, can be included in an initial charge and then (A) and/or (B) added to that initial charge, or (A) or (B), at least in part, can be included in an initial charge, (C) can be added, and then the last component can be added.

5

The course of the reaction can be monitored by determining the NCO content by means, for example, of titrimetry. When the target NCO content has been reached the reaction is terminated. In the case of a purely thermal reaction regime, this can be done, for

- 10 example, by cooling the reaction mixture to room temperature. Where a catalyst of the aforementioned type is used, however, the reaction is generally stopped by adding suitable deactivators. Examples of suitable deactivators include organic or inorganic acids, the corresponding acid halides, and alkylating agents.
- 15 Examples that may be mentioned include phosphoric acid, monochloroacetic acid, dodecylbenzenesulfonic acid, benzoyl chloride, dimethyl sulfate, and, preferably, dibutyl phosphate and also di-2-ethylhexyl phosphate. The deactivators can be used in amounts of from 1 to 200 mol%, preferably from 20 to 100 mol%,
- 20 based on the number of moles of catalyst.

The resultant polyisocyanate mixtures generally have an NCO content of preferably 6.0 to 23.0% by weight, more preferably 8.5 to 22.0% by weight.

25

The resulting polyisocyanate mixtures generally have a viscosity at 23°C of preferably 0.2 to 20 Pas, more preferably 0.5 to 8 Pas.

- The process may be carried out where appropriate in a suitable
- 30 solvent (D) which is inert toward isocyanate groups. Examples of suitable solvents are the conventional paint solvents known per se, such as ethyl acetate, butyl acetate, ethylene glycol monomethyl or monoethyl ether acetate, 1-methoxy-2-propyl acetate, 3-methoxy-n-butyl acetate, acetone, 2-butanone,
- 35 iso-butyl methyl ketone, 4-methyl-2-pentanone, cyclohexanone, cyclopentanone, toluene, xylene, chlorobenzene, white spirit, aromatics with relatively high degrees of substitution, such as are sold, for example, under the names Solventnaphtha®, Solvesso®, Shellsol®, Isopar®, Nappar® and Diasol®, propylene
- 40 glycol diacetate, diethylene glycol dimethyl ether, dipropylene glycol dimethyl ether, diethylene glycol ethyl and butyl ether acetate, N-methylpyrrolidone, and N-methylcaprolactam, and also, preferably, carbonic esters or lactones, which are specified in EP-A1 697 424, page 4 lines 4 to 32, more preferably dimethyl
- 45 carbonate, diethyl carbonate, 1,2-ethylene carbonate and 1,2-propylene carbonate, lactones such as  $\beta$ -propiolactone,

$\gamma$ -butyrolactone,  $\epsilon$ -caprolactone, and  $\epsilon$ -methylcaprolactone, or else any desired mixtures of such solvents.

It is also possible first to prepare the isocyanates of the  
5 invention without solvent and then to use a solvent (D) to take up the product thus obtainable.

The mixtures of the invention preferably comprise in solvent-free form

10

- (A) 30 - 90%, preferably 50 to 90%, by weight,
- (B) 5 - 60%, preferably 5 - 50%, by weight, and
- (C) 5 - 40%, preferably 5 - 50%, by weight,

15 the sum of (A), (B), and (C) making 100% by weight.

Based on the total mixture, the solvent (D) may be present in amounts of from 0 to 60% by weight, preferably in amounts of from 0 to 50% by weight.

20

The mixtures of the invention may be dispersed preferably in water for the purpose of preparing aqueous dispersions; with particular preference, the mixtures of the invention are mixed into aqueous dispersions.

25

The polyisocyanate formulation of the invention is suitable for modifying aqueous coating materials (paints, protective coatings) for substrates such as wood, wood veneer, paper, paperboard, cardboard, textile, leather, nonwoven, plastics surfaces, glass,  
30 ceramic, mineral building materials such as cement moldings and fiber cement slabs, coated or uncoated metals, adhesives or impregnating compositions, for dyeing, for example, based on aqueous dispersions or solutions with a solids content of from 5 to 40% by weight, preferably from 5 to 20% by weight. Suitable  
35 coating materials include the aqueous dispersions, known per se, of homopolymers and copolymers of olefinically unsaturated monomers or polyurethanes or else solutions of natural substances, such as of casein, for example.

40 The polyisocyanate formulations of the invention are added to the aqueous coating materials generally in an amount of 1 to 25% by weight, preferably from 2.5 to 20% by weight, based on the solids content of the coating material.

45 They are applied to the substrate in a known manner by means, for example, of spraying at a rate of from 5 to 50 g solids/m<sup>2</sup>.

Suitable dispersions of homopolymers or copolymers of olefinically unsaturated monomers are, for example, conventional dispersions of homopolymers or copolymers based on vinyl esters of carboxylic acids having 2 to 18, preferably 2 to 4, carbon atoms such as vinyl acetate in particular, where appropriate with up to 70% by weight, based on the total amount of olefinically unsaturated monomers, of other olefinically unsaturated monomers, and/or of homopolymers or copolymers of (meth)acrylic esters of alcohols having 1 to 18, preferably 1 to 4, carbon atoms, such as (meth)acrylic acid, methyl, ethyl, propyl, hydroxyethyl or hydroxypropyl esters in particular, together where appropriate with up to 70% by weight of other olefinically unsaturated monomers, and/or butadiene-styrene copolymers having a butadiene content of about 20 to 60% by weight, and/or of other diene polymers or copolymers such as polybutadiene or copolymers of butadiene with other olefinically unsaturated monomers such as styrene, acrylonitrile and/or methacrylonitrile, for example, and/or aqueous dispersions of polymers or copolymers of 2-chloro-1,3-butadiene, where appropriate with other olefinically unsaturated monomers of the type exemplified above, e.g., those with a chlorine content of about 30 to 40% by weight, in particular a chlorine content of about 36% by weight.

Preference is given to aqueous dispersions of copolymers of 90 to 99.5% by weight of acrylates or methacrylates of alkanols containing 1 to 4 carbon atoms and 0.5 to 10% by weight, based in each case on the copolymer, of hydroxyalkyl acrylates and methacrylates having 2 to 20 carbon atoms in the hydroxyalkyl radical, such as hydroxyethyl, hydroxypropyl or hydroxybutyl acrylate or methacrylate. Such dispersions are known per se and can be prepared conventionally by emulsion polymerization (see Houben-Weyl, Methoden der organischen Chemie, 4th edition, vol. E 20, p. 217 ff.).

Suitable aqueous polyurethane dispersions are those of the type known per se, as described in, for example, US-A 3,479,310, GB-A 1,076,688, US-A 4,108,814, US-A 4,092,286, DE-A 2 651 505, US-A 4,190,566, DE-A 2 732 131 or DE-A 2 811 148.

The aqueous dispersions used may comprise the customary auxiliaries and additives. These include, for example, fillers, such as quartz powder, quartz sand, highly dispersed silica, heavy spar, calcium carbonate, chalk, dolomite or talc, which are often used together with suitable wetting agents such as polyphosphates, for example, such as sodium hexametaphosphate, naphthalenesulfonic acid, ammonium or sodium salts of polyacrylic

acids, the wetting agents being added generally in amounts of from 0.2 to 0.6% by weight, based on filler.

Further suitable auxiliaries are organic thickeners to be used in amounts, for example, of from 0.01 to 1% by weight, based on the dispersion, such as cellulose derivatives, alginates, starch or starch derivatives or polyacrylic acid, or inorganic thickeners to be used in amounts of from 0.05 to 5% by weight, based on the dispersion, such as bentonites, for example.

10 Fungicides for preservation may also be added to the dispersions. These are employed generally in amounts of from 0.02 to 1% by weight, based on the dispersion. Examples of suitable fungicides are phenol and cresol derivatives and also organotin compounds.

15 Substrates for impregnation are, for example, synthetic or nonsynthetic fibers and/or woven or nonwoven fabrics comprising such fibers.

20 The mixtures of the invention can be dispersed very finely in aqueous dispersions. The resulting dispersions are very stable on storage. Moreover, little of the water-emulsifiable polyisocyanate need be added in order to set the desired properties of the dispersion or to achieve the desired properties during application.

25 The mixtures of the invention can of course be provided with customary auxiliaries and additives of coatings technology. These include, for example, defoamers, thickeners, leveling assistants, pigments, emulsifiers, dispersing assistants, and also solvents. The desired processing viscosity is set by adding water.

To prepare the dispersions it is sufficient in the majority of cases to use simple emulsifying techniques, for example, with a mechanical stirrer, or else in many cases simple mixing of the two components by hand, in order to obtain dispersions having very good properties. Naturally it is also possible, however, to employ mixing techniques involving a relatively high shearing energy, such as jet dispersion, for example.

40 The coating materials comprising the mixtures of the invention may be used in particular as primers, surfacers, pigmented topcoat materials, and clearcoat materials in the sector of automotive refinishing or the painting of large-size vehicles. The coating materials are particularly suitable for applications where particularly high application reliability, outdoor weathering stability, optical properties, solvent resistance,

chemical resistance, and water resistance are required, such as in automotive refinishing and the painting of large-size vehicles.

- 5 The coating materials comprising the mixtures of the invention may be applied by any of a wide variety of spraying methods, such as, for example, air-pressure, airless or electrostatic spraying methods using one-component or two-component spraying units, or else by spraying, troweling, knife coating, brushing, rolling, roller coating, flow coating, laminating, in-mold coating or coextrusion.

The coatings are generally dried and cured under normal temperature conditions, i.e., without heating the coating.

- 15 Alternatively, the mixtures of the invention may be used to produce coatings which following application are dried and cured at elevated temperature, e.g., at 40 - 250°C, preferably 40 - 150°C, and especially from 40 to 100°C.
- 20 Despite the fact that certain publications relating to the preparation of water-emulsifiable polyisocyanates, such as DE-A1 40 01 783, EP-A2 206 059, EP-A2 486 881, EP-A1 540 985 or DE-A1 199 58 170, include mixtures of isocyanurates and/or biurets of 1,6-diisocyanatohexane (HDI) and isocyanurates of 1-isocyanato-3,5,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI)
- 25 with emulsifiers within long lists of suitable starting isocyanates, it was impossible for the skilled worker to infer from any of the abovementioned publications any specific indication whatsoever that the mixtures according to the invention exhibit improved hardness, an improved increase in hardness, and a ready emulsifiability at the same time. Moreover, as compared with the prior art, the mixtures according to the invention exhibit a longer "potlife", this being the period of time within which a batch remains usable after all of the
- 30 constituents have been mixed, and does not, for example, undergo separation or premature curing.

The examples which follow are intended to illustrate the properties of the invention but without restricting it.

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#### Examples

In this specification, unless indicated otherwise, parts are to be understood as meaning parts by weight.

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#### Tests



All specimens were tested in the formulation given below:

#### Binder dispersion

- 5 240 p Daotan® 1225 (from Solutia)
- 119 p Plusaqua® V 608 (from Omya)
- 310 p distilled water
- 18 p Fluorad® FC 430 (from 3M)
- 9 p AMP 90 (from Angus Chemie)

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One part of the polyisocyanate was added with stirring to one part of this binder dispersion (amounts relate to nonvolatile weight fractions).

- 15 The finished emulsion was applied with a 200 µm doctor blade to a degreased metal panel and was flashed off at room temperature for 20 minutes before the painted panel was baked in a gradient oven for 30 minutes. Prior to testing, the finished panels were stored for 24 hours under standard conditions (50% humidity, 23°C). The
- 20 hardness of the paint films was then measured by means of a pendulum damping test in accordance with DIN 53157 (König hardness). Measurements are indicated in pendulum swings (the higher the number of pendulum swings, the harder the paint film).

#### 25 Isocyanate A1:

HDI isocyanurate having an NCO content of 22.2% and a viscosity at 23°C of 2.8 Pas

#### 30 Isocyanate B:

IPDI isocyanurate having an NCO content of 17.2% (Vestanat® T 1890/100 from Degussa)

#### 35 Abbreviations:

- HDI hexamethylene diisocyanate
  - IPDI isophorone diisocyanate
  - PC propylene carbonate
  - 40 T parts by weight
- Example 1 - Hydrophilized isocyanate = polyisocyanate a1

- 26 g (0.146 mol) of a mixture of 80 parts 2,4-tolylene diisocyanate and 20 parts 2,6-tolylene diisocyanate were added to
- 45 150 g (0.30 mol) of a monofunctional polyethylene oxide with an OH number of 112, prepared starting from methanol, at 60°C and the mixture was stirred for 60 minutes (= c2). The emulsifier thus

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obtained was cooled to 30°C and 900 g of isocyanate A1 were stirred in. This gives a water-emulsifiable polyisocyanate (= a1) having an NCO content of 18.4% and a viscosity at 23°C of 3.0 Pas.

- 5 Isocyanate a1, isocyanat B, and propylene carbonate were mixed in the proportions indicated in the table.

10	Example No. 1	Isocyanate a1	Isocyanate B	PC	NCO content
		(g)	(g)	(g)	(%)
	1	28	5	22	10.9
	2	24.5	7.5	21.33	10.8
	3	21	10	20.67	10.8
	4	17.5	12.5	20	10.7
15	Comparative, C	30	./.	20	11.0

Results: example 1

20	Baking temp. [°C]	Pendulum damping				V
		1	2	3	4	
	60	44	41	43	52	26
	70	67	68	64	74	36
	80	93	87	107	105	42
	90	98	108	122	124	45
25	100	121	126	126	136	47
	110	125	128	130	138	53
	120	126	131	131	140	94
	130	126	132	132	141	99
	140	126	132	136	141	99
30	150	130	132	138	141	101

Example 2

solvent-containing hydrophilicized isocyanate B = isocyanate b1

- 35 14 g (0.014 mol) of a monofunctional polyethylene oxide of molecular mass of 1 000, prepared starting from methanol, are added to a solution of 125 g (0.51 eq NCO) of isocyanate B in 53.6 g of Solvesso® 100 (about 28% by weight). The mixture is stirred at 85°C for 3 hours and, after cooling, gives a turbid, viscous paste having an NCO content of 11% (= b1), which with considerable mechanical effort can be converted into an aqueous, coarse emulsion.

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By preparing mixtures of hydrophilicized isocyanate b1 and of the hydrophilicized isocyanate a1 described in example 1, with the addition of propylene carbonate, a readily emulsifiable isocyanate mixture is obtained which results in a fine emulsion.

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10	Example No. 2	Isocyanate a1 (% by weight)	Isocyanate b1 (% by weight)	PC (% by weight)	NCO content (%)
	1	56	24	20	12.9
	2	60	20	20	12.9
	3	68	12	20	13.1
	4	76	4	20	13.4
15	Comparative, C	80	-	20	13.5

Results example No. 2

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20		Pendulum damping				
	Baking temp. [°C]	1	2	3	4	C
25	60	37	29	21	27	19
	70	64	58	48	51	40
	80	76	88	72	78	59
	90	94	109	87	89	76
	100	99	114	95	91	85
	110	105	119	96	92	86
	120	108	122	99	97	85

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